Polyurethanes: Products of 4,4′-Bis(6-hydroxyhexylthio)diphenyl Ether and Methylene Bis(4-phenyl isocyanate)

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ABSTRACT: New linear polyurethanes derived from 4,4′-bis(6-hydroxyhexylthio)diphenyl ether and methylene bis(4-phenyl isocyanate) were synthesized by either melt or solution polymerization with a strictly equimolar ratio of the monomers. In the solution method, good results were obtained with the aprotic solvent *N,N*-dimethylformamide at an approximately 20 wt % concentration of the monomers, with dibutyltin dilaurate as a catalyst, the process being conducted at 90–100°C for 4 h. The basic physicochemical properties of the polymers were investigated with thermogravimetric analysis and differential scanning calorimetry. The molecular weight distribution was determined by gel permeation chromatography. Shore hardness and tensile test results were also examined. The structures of the resulting products were confirmed with elemental analysis, Fourier transform infrared, and X-ray diffractometry. The properties of the copolyurethanes, containing various amounts of poly(oxytetramethylene) diol (~1000) or polycaprolactone diol (~1250) and synthesized under the conditions for the nonsegmented polyurethanes, were also examined. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 380–388, 2003

Key words: linear polyurethanes; polyaddition; nonsegmented polyurethanes; segmented polyurethanes; characterization

INTRODUCTION

Generally, the properties of polyurethanes (PUs) depend on many factors, including the structure, the hard and soft segments, the hydrogen bonds, the phase separation, the molecular weight, and the method of synthesis.[1–8] The amount of hard segments has a great influence on the modulus of elasticity, hardness, tensile strength, and maximum temperature of their use. Soft segments in hard segments (the dispersed phase) are of much greater importance than hard impurities in the continuous soft phase. PUs, with low contents of hard segments, can show good elastic properties and higher elongation at break. Urethane groups in PUs form hydrogen bonds as a result of interactions of NH with CO in urethane or urea groups and, to a small extent, with ether or ester groups of soft segments. PUs exhibit good mechanical properties as a result of the microphase separation of hard and soft segments. The structure of NCO groups naturally changes the behavior of hard segments,[9–13] The molecular weight of PUs depends on the synthesis method and influences the value of the glass-transition temperature (T_g). Polyaddition in the melt, contrary to the solution method, produces PUs with narrow molecular weight distributions of hard-segment sequences.

In previous articles,[14–18] we described the synthesis of PUs with good chemical and thermal properties that were obtained from 4,4′-bis(4-hydroxyethylthio)-, 4,4′-bis(4-hydroxyethoxy)-, and 4,4′-bis(6-hydroxyhexoxy)diphenyl ethers with aromatic or aliphatic diisocyanates [1,6-hexamethylene diisocyanate (HDI), methylene bis(4-phenyl isocyanate) (MDI; Aldrich, Steinheim, Germany), or tolylene diisocyanate (TDI)]. The properties of these PUs largely depended on the presence of a catalyst, the types and molar ratios of the monomers, and the temperature of the polyaddition reaction. This article deals with the preparation and properties of aromatic and aliphatic PUs with 4,4′-bis(6-hydroxyhexylthio)diphenyl ether (HHPE) and MDI, in melt or in solution, with or without a catalyst. In the next stage, segmented PUs were obtained by two methods from HHPE, MDI, and poly(oxytetramethylene) diol (PTMO; ~1000) or polycaprolactone diol (PCD; ~1250). The modifiers were used in amounts of 20, 40, 60, and 80 mol % in relation to HHPE under the conditions established earlier for nonsegmented PUs.

EXPERIMENTAL

Materials

Dibutyltin dilaurate (DLDBT; Merck, Darmstadt, Germany) was used as received. *N,N*-Dimethylformamide (DMF; Merck) was distilled and dried over 3-Å molecular sieves. MDI (Farbenfabriken Bayer AG) was

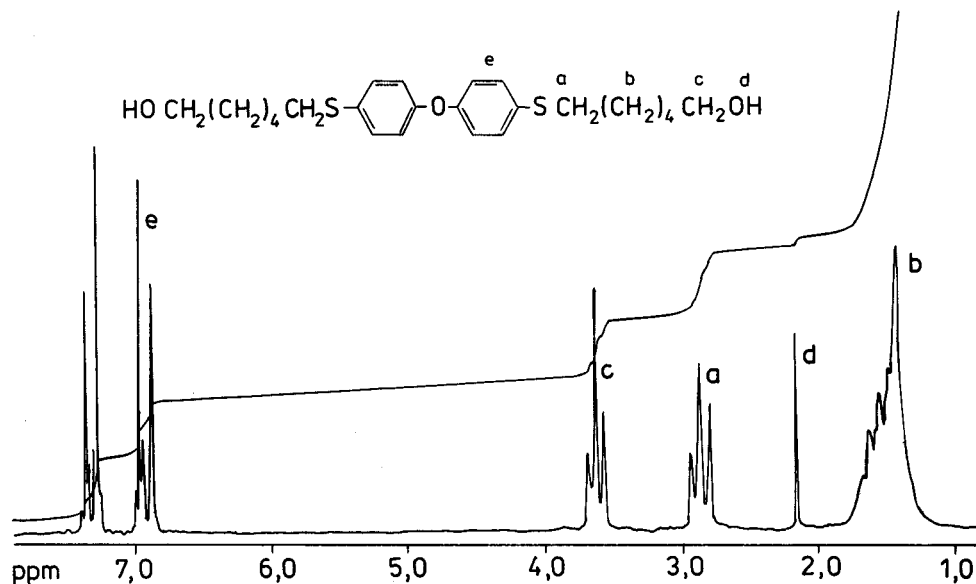*Correspondence to:* D. Wdowicka (wdowd@hermes.umcs.lublin.pl).

Figure 1 ¹H-NMR spectrum of HHPE.

purified by vacuum distillation. The distillation fraction at 148–150°C and 0.12 mmHg was collected.

Monomer synthesis

The initial HHPE was obtained by the reaction of bis(4-mercaptophenyl)ether (MPE) with 6-chloro-1-hexanol in an ethanol solution of sodium hydroxide as follows. MPE (4.68 g, 0.02 mol) was dissolved in 80 mL of a 20% aqueous solution of sodium hydroxide, and to the resulting solution, 8.2197 g (0.045 mol) of 6-chloro-1-hexanol in 15 mL of ethanol was added. The oil product resulted in an upper layer that solidified after cooling and was recrystallized from benzene (80 mL); this yielded plates.

mp: 71–72°C. Yield: 7.8 g (87.12%). ELEM. ANAL. Calcd. for $C_{24}H_{34}O_3S_2$: C, 66.31%; H, 7.90%. Found: C, 66.70%; H, 7.99%.
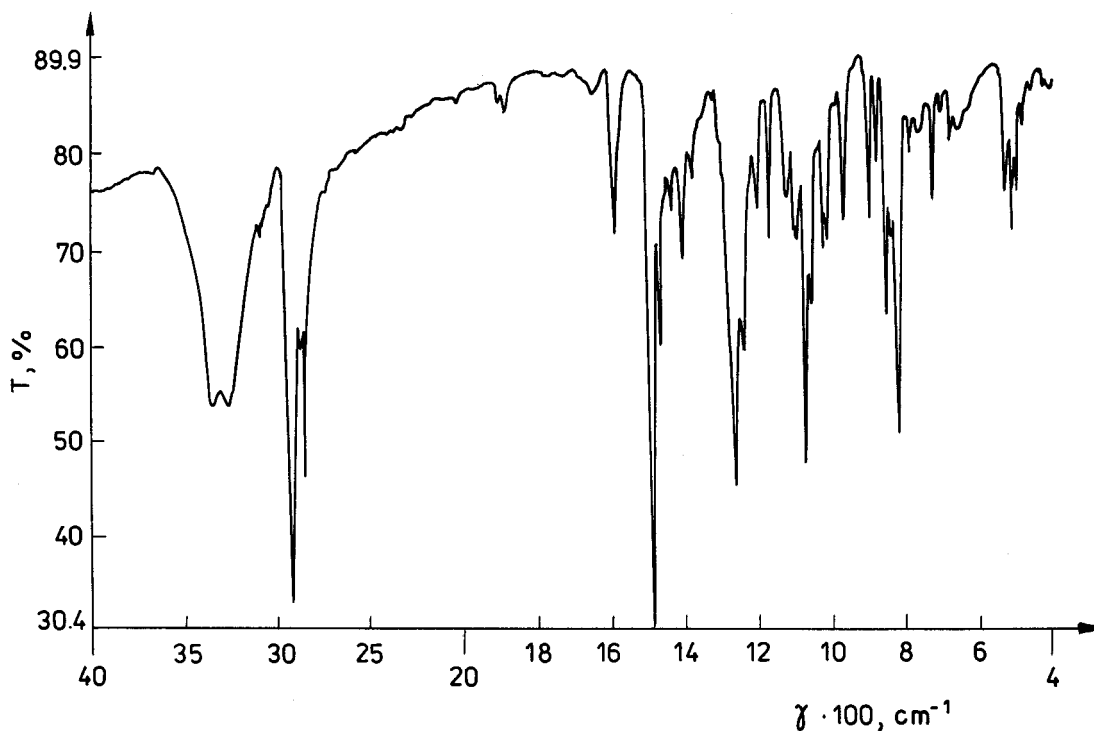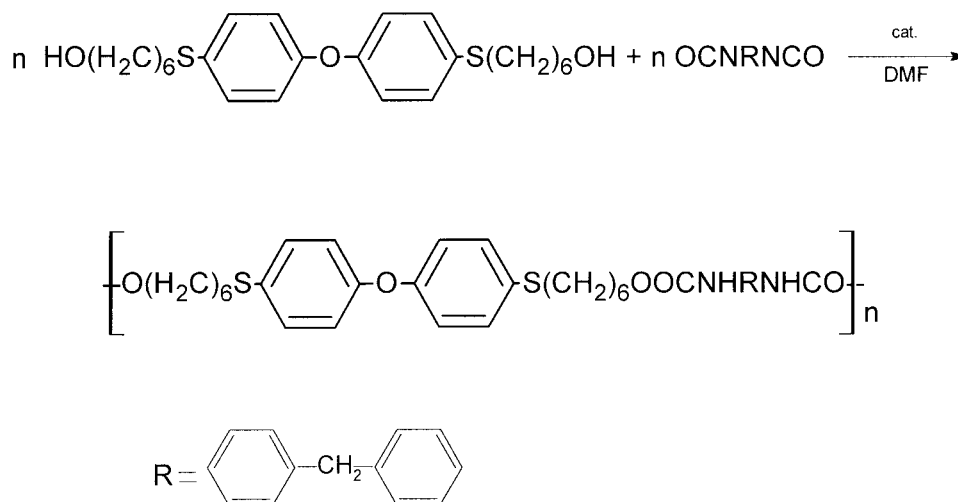

Figure 2 FTIR spectrum of HHPE.

Scheme 1

The structure of the newly obtained diol is shown in Figures 1 and 2.

Fourier transform infrared (FTIR; KBr, cm^{-1}): 3244 (OH$\cdots$O stretching, s), 2923 (CH$_2$, asymmetric), 2852 (CH$_2$, symmetric), 1491 (benzene ring, m), 1073 (C—O stretching, primary alcohol), 1264 (diphenyl ether). ^{1}H-NMR (CDCl$_3$, ppm): 1.43–1.70 [m, 16H (CH$_2$)$_4$], 2.17 (s, 2H, OH), 2.69–2.95 (t, 4H —SCH_2CH$_2$—, J = 7.05 Hz), 3.59–3.76 (t, 4H, —CH_2OH, J = 6.2 Hz), 6.93, 7.32 (d, d, 8H, Ar—H, J = 8.5 Hz).

Polymer synthesis

The PUs were obtained with a strictly equimolar ratio of the dihydroxyl compound to the diisocyanate by both melt and solution polymerization, with or without a catalyst.

Melt polymerization

A typical procedure for the synthesis of PUs was as follows. In a dry, four-necked, round-bottom flask fitted with a condenser, a mechanical stirrer, a thermometer, and a nitrogen inlet tube, 4.3427 g (0.01 mol) of HHPE and 2.50 g (0.01 mol) of MDI were placed, and they were gradually heated in a oil bath under a dry N$_2$ atmosphere until a clear solution appeared (ca. 80°C). Two drops of DLDBT were added, and during vigorous stirring, the polymerization rapidly began after 120°C was reached. A light yellow, hard product was obtained. The reaction without a catalyst required about 2 h of heating.

Solution polymerization

With the same apparatus previously described, 2.1713 g (0.005 mol) of HHPE and 10 mL of freshly distilled DMF with three drops of DLDBT were used. Nitrogen
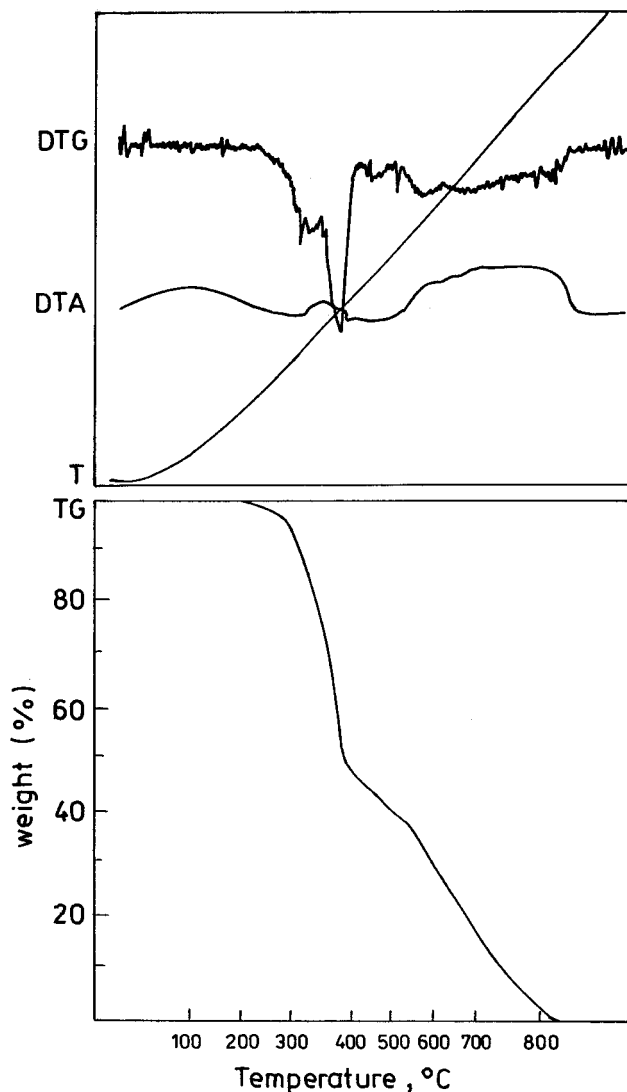

Figure 3 TGA and DTA of PU-1 [heating time in air = 100 min (measurement relative to Al$_2$O$_3$); heating rate = 10°C/ min; amount of PU-1 = 100 mg].
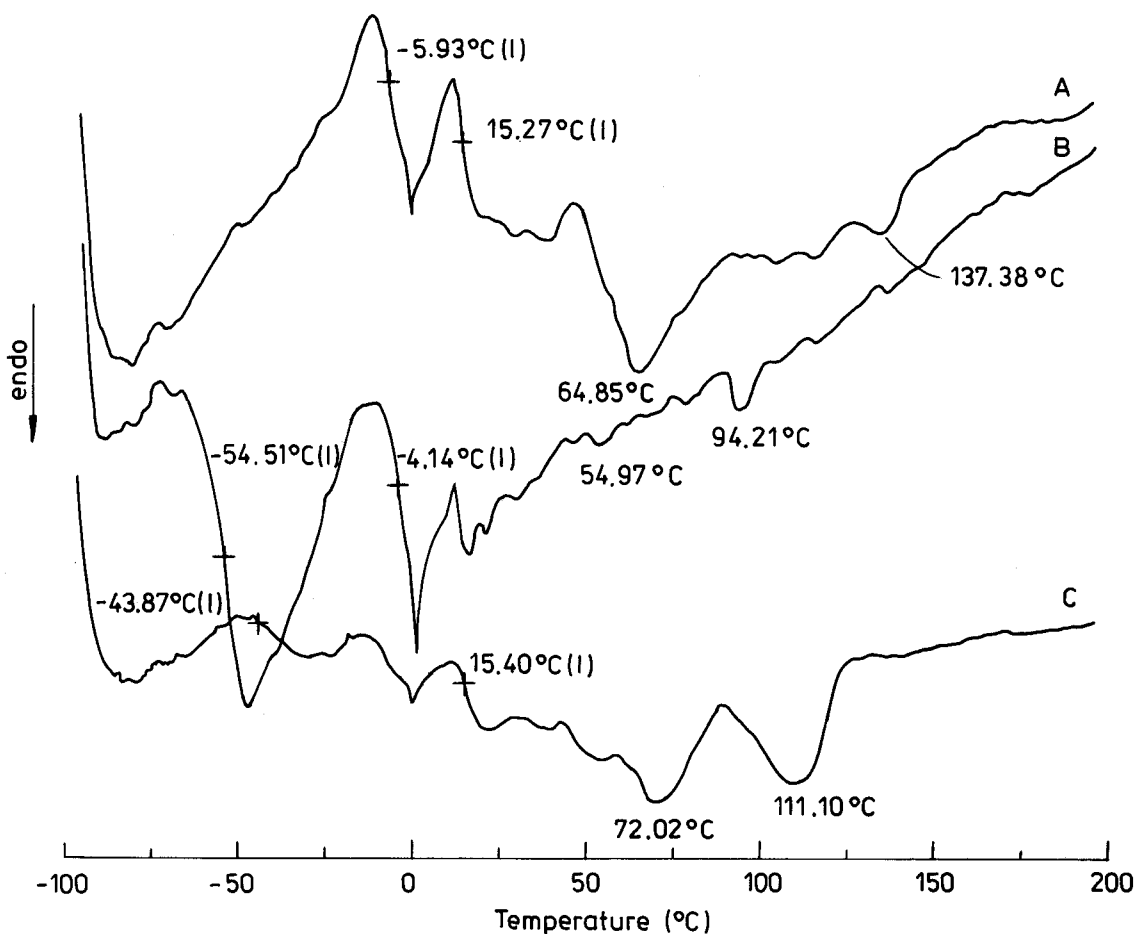
Figure 4 DSC thermograms of (A) PU-1, (B) PU-40P, and (C) PU-40P$_1$.

flowed continuously through the system. Then, as the temperature was raised to 90°C, 1.25 g (0.005 mol) of MDI in 5 mL of DMF was added dropwise to this solution over a period of 10 min with vigorous stirring. The contents were kept at this temperature for 4 h until the reaction was completed. The warm, viscous solution was then poured into 100 mL of cold methanol to precipitate the polymer in the form of a pale yellow, rubberlike product. The polymer was filtered off, washed with hot methanol, and dried *in vacuo* at 100°C for 10 h. The yield was 2.94 g (85.98%).

ELEM. ANAL. Calcd.: C, 68.92%; H, 5.74%; N, 4.12%. Found: C, 69.52%; H, 6.24%; N, 4.45%.

Segmented polymer synthesis

Copolyurethanes (CPUs) were obtained in the melt or in solution, and an example is given for a polymer containing 20 mol % PTMO. The apparatus was the same as that described previously for the synthesis of nonsegmented polymers, and the amounts of the monomers were as follows: 2.5 g (0.01 mol) of MDI, 3.4582 g (0.008 mol) of HHPE, and 2 g (0.002 mol) of

PTMO. The rest of the procedure was the same as that described previously.

Polymer characterization

Spectroscopy

FTIR spectra were obtained with a PerkinElmer 1725 (Beaconsfield, Buckinghamshire, England) FTIR spectrophotometer with KBr discs or thin films, as appropriate.

Viscosity

The reduced viscosity (η_{red}) of 1% solutions of the polymers in phenol/tetrachloroethane (CCE) mixtures with a weight ratio of 1:3 was measured by a Ubbelohde viscometer at 25°C.

Molecular weight

The molecular weights were obtained with a Knauer (Berlin, Germany) gel permeation chromatography
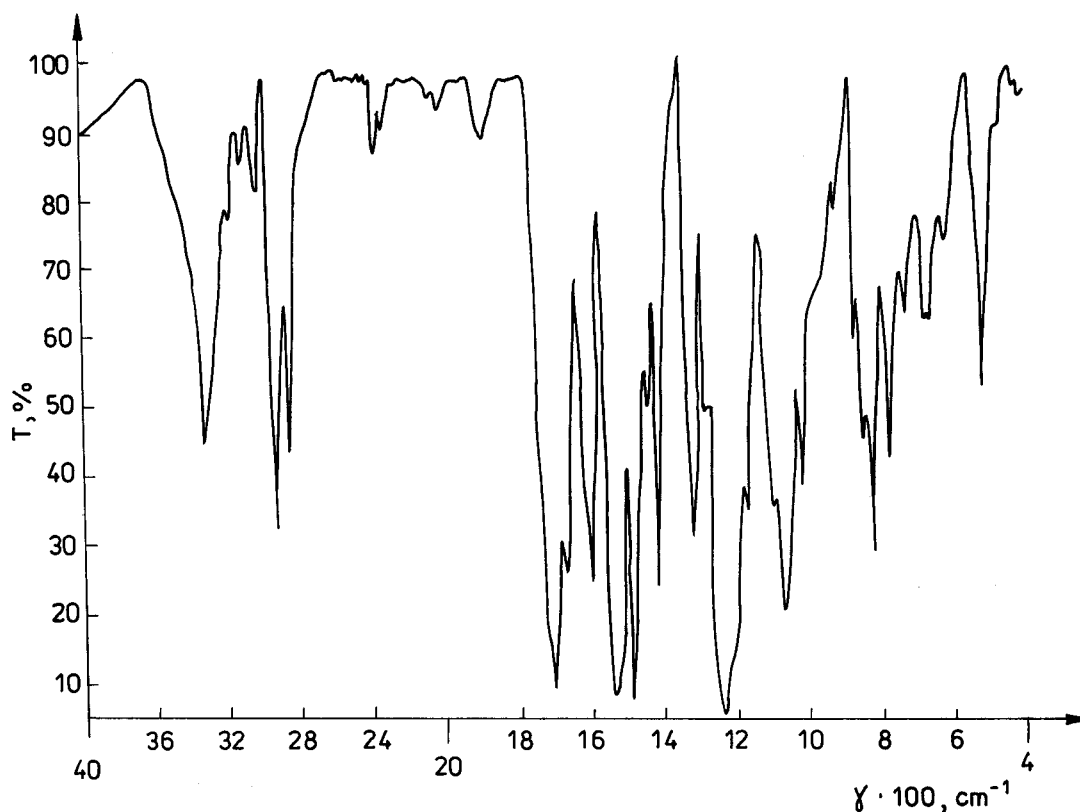
Figure 5 FTIR spectrum of PU-1.

(GPC) instrument equipped with 10^6-, 10^5-, 10^4-, 10^3-, and 10^2-Å and 50-μm PL-gel columns and a refractometric detector. Tetrahydrofuran (THF) was used as the eluent (flow rate = 1.0 mL/min), and numerical values for the molecular weights were obtained in comparison with polystyrene standards.

Thermogravimetric analysis (TGA)

The TGA characteristics were measured on an MOM 30427 derivatograph (F. Paulik, J. Paulik, and L. Erdey, Budapest, Hungary) at a heating rate of 10°C/min in air.

T_g

Differential scanning calorimetry (DSC) thermograms were obtained with a DuPont 2000 TA (U.S.) calorimeter at a heating rate of 10°C/min, and T_g was determined as the temperature of the inflection point on the curves describing the rate of heat capacity changes.

Hardness

The hardness of the PUs was measured with Shore A and D durometers at 25°C. Values were taken after 15 s.

Tensile testing

Tensile testing was performed with an TIRA Test 2200 (VEB WMK, FRITZ Heckert, Chemnitz, Germany) universal testing machine at a speed of 50 mm/min at 23°C. Tensile test pieces, 1 mm thick and 7 mm wide (for the section measured), were cut from pressed sheets. The results reported are the median values for three replicates.

X-ray analysis

Diffraction measurements were performed with a DRON-3 X-ray apparatus (Burieviestnik, Russia) with a Cu tube and a Ni filter. X-ray patterns of the investigated samples were obtained from the number of impulses within an angle greater than 10°.

RESULTS AND DISCUSSION

Scheme 1 depicts the synthesis of the nonsegmented PUs, which were prepared easily by both melt and solution methods through the reaction of HHPE with MDI, with or without a catalyst.

MDI was chosen from the aromatic diisocyanates because of its ready availability and symmetrical structure. The nonsegmented PUs were hard products
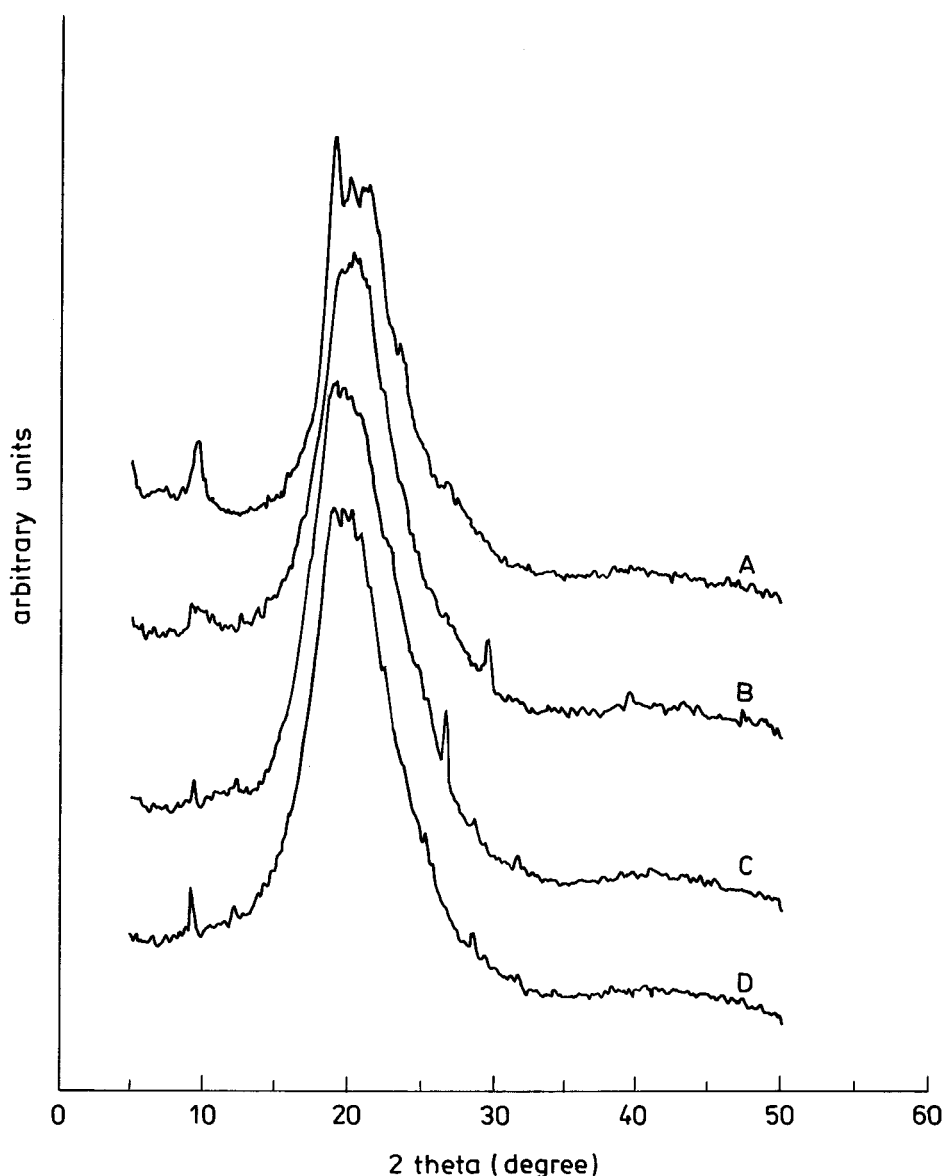
Figure 6   X-ray patterns: (A) PU-1, (B) PU-20P, (C) PU-40P, and (D) PU-60P.

TABLE I
Reduced Viscosities and Molecular Weights of CPUs

CPU	η_{red} (dL/g)	GPC data		
		$\bar{M}_n \times 10^3$	$\bar{M}_w \times 10^3$	$\bar{M}_w/\bar{M}_n$
PU-20P	0.32	8.21	17.97	2.19
PU-40P	0.38	11.25	23.96	2.13
PU-60P	0.46	13.34	26.11	1.96
PU-80P	0.54	17.73	41.63	2.35
PU-20P$_1$	0.26	8.44	17.22	2.04
PU-40P$_1$	0.32	13.49	31.72	2.35
PU-60P$_1$	0.39	15.14	31.37	2.07
PU-80P$_1$	0.42	16.41	38.48	2.34

Codes of CPUs. Examples: PU-20P–CPU was obtained from HHPE and 20 mol % PTMO (~1000); PU-20P$_1$–CUP was obtained from 20 mol % PCD (~1250).

insoluble in common organic solvents, having melting points (T_m's) of 216–222°C and good thermal and chemical stability. The thermal stability was measured with dynamic thermal analysis (DTA) and DSC methods, and the results are presented in Figures 3 and 4. The initial decomposition began at 250°C, and its 5% weight loss, taken as the criterion for thermal stability, as shown later in Table II, began at 290°C for the examined polymer. The structure of the resulting PUs was confirmed with elemental analysis, FTIR spectra (Fig. 5), and X-ray diffraction (Fig. 6).

The elemental analysis values of the PUs agreed well with those calculated for the proposed structure (Scheme 1), as was expected. As shown in Figure 5, the FTIR spectrum of the polymer shows the characteristic absorption of the C=O bond of the urethane group at 1684–1625 cm^{-1}, the —NH stretching of the urethane

TABLE II
Thermal Properties of PUs

PU	T_g (°C)	T_m (°C)	ΔH^a (J/g)	Mass loss (%) 5	10	20
	−5.93	64.85	5.15			
PU-1	15.27	106.39	0.66	290	320	350
		137.38	0.43			
		51.75	1.86			
PU-20P	0.00	102.03	10.76			
		118.16	1.52			
PU-40P	−54.51	54.97	0.11	320	340	370
	−4.14	94.21	0.32			
PU-60P	−0.02	21.91	2.79			
		89.75	12.85			
PU-80P	−54.64	61.66	5.78	330	350	390
	13.82					
PU-20P$_1$	−44.92	83.65	2.57			
	44.00	117.29	8.42			
PU-40P$_1$	−43.87	72.02	3.42	290	310	340
	15.40	111.10	6.36			
		21.77	10.47			
PU-60P$_1$	−34.86	37.99	8.92			
		72.03				
PU-80P$_1$	−28.13	40.67	31.02	320	340	370

^{a} H = heat of fusion.

group at 3500–3100 cm^{-1}, the —NH bending vibration of the urethane group at 1577–1538 cm^{-1} and the —CH$_2$— stretching at 2960 cm^{-1}. The band of —NCO at 2270 cm^{-1} cannot be seen.

At the next stage, we obtained segmented PUs by two methods from HHPE, MDI, and PTMO (~1000) or PCD (~1250), using the polyether diol or polyester diol in amounts of 20, 40, 60, and 80 mol % with respect to HHPE. CPUs, obtained in the melt, turned out to be strong, waxlike, pale yellow products insoluble in common organic solvents. The CPUs containing more than 60 mol % soft segments derived from PTMO or PCD were soluble in a phenol and CCE mixture, with high values of η_{red} of about 3.80 and 4.20 dL/g, respectively, which indicated the high molecular weights of these polymers. However, CPUs obtained by the solution method were pale yellow thermoplastic elastomers with T_m's of 60–140°C for the PUs obtained from PTMO and 40–118°C for poly(ester urethane)s. These segmented PUs, contrary to nonsegmented ones, were soluble in DMF, DMSO, CCE, and THF; therefore, the determination of their molecular weights was possible. The η_{red} values of these polymers, as we can see in Table I, were 0.32–0.54 dL/g, corresponding to number-average molecular weights (M_n) of 8210–17,730. The molecular weight distributions [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of these samples were narrow for all the examined polymers.

The thermal properties of the chosen segmented PUs presented in Table II were the same or higher than those of the nonsegmented ones, and their 5% weight loss occurred at 290–330°C. Typical DSC scans for the chosen samples of the CPUs are presented in Figure 4, and the thermal data are given in Table II. As can be seen, the increasing number of soft segments in the polymer structure in some cases considerably influenced T_g. Therefore, these parameters were 0 to −54°C for the poly(ether urethane)s. The nearly same values of T_g, about −54°C, for the PTMO series containing 40 or 80 mol % soft segments point to the immiscibility between the hard and soft segments resulting from the good phase separation of these segments. For the poly(ester urethane)s, T_g ranged from −44 to −28°C, depending on the number of soft segments derived from PCD. The observed increase in T_g was due to the fact that the hard-segment units were hydrogen-bonded to ester groups of PCD soft segments, and they resulted from phase mixing. The

TABLE III
Mechanical Properties of PUs

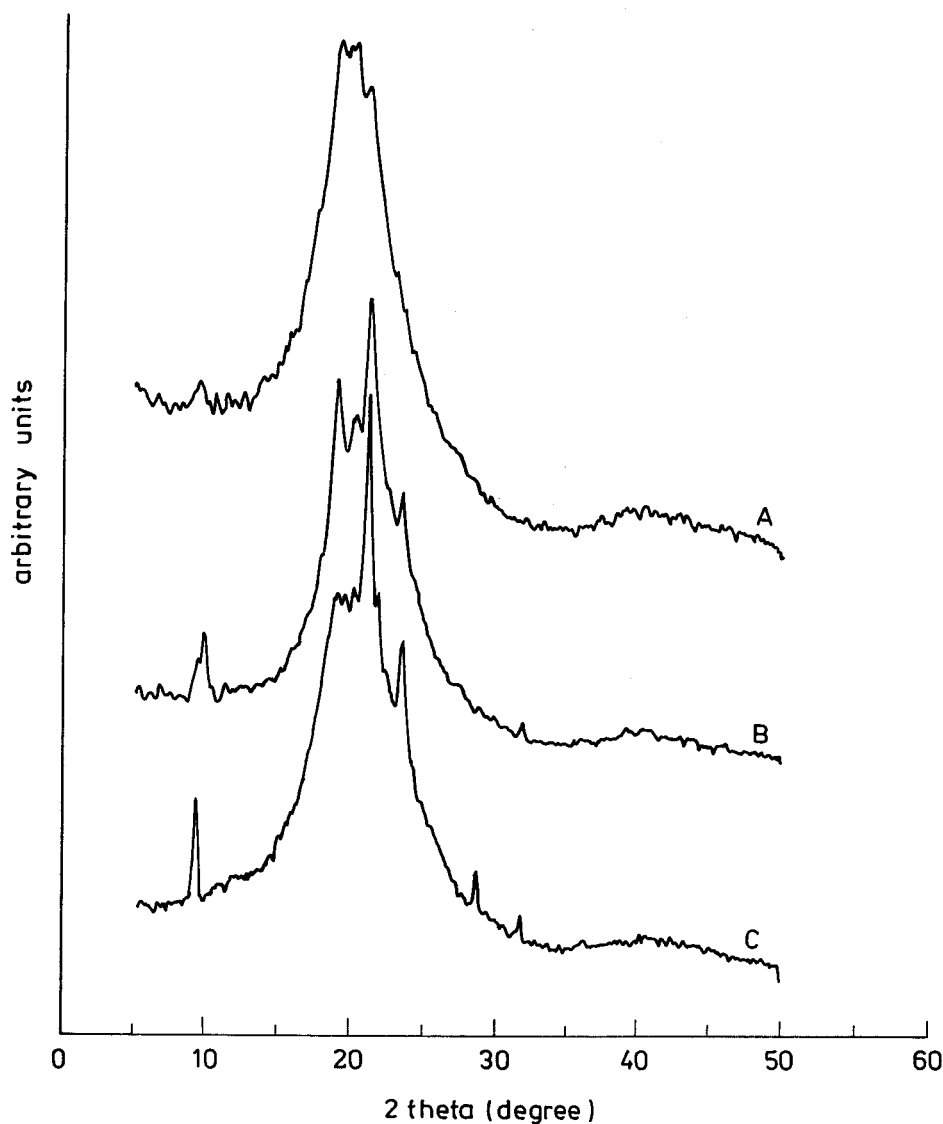| PU	Hardness (shore A/D)	Modulus of elasticity (MPa)	Tensile strength (MPa)	Elongation at break (%)
PU-1	96/50	58.34	17.84	40.62
PU-20P	90/41	12.54	31.55	578.73
PU-40P	88/27	7.35	23.25	935.04
PU-60P	70/14	7.26	12.62	1125.30
PU-80P	62/12	2.34	8.62	1208.19
PU-20P$_1$	89/26	3.65	19.11	572.23
PU-40P$_1$	86/22	2.64	15.57	468.85
PU-60P$_1$	72/11	2.85	9.92	320.25
PU-80P$_1$	68/14	5.48	5.29	280.60

Figure 7 X-ray patterns: (A) PU-20P$_1$, (B) PU-40P$_1$, and (C) PU-60P$_1$.

highest enthalpy of fusion, about 31 J/g, for a CPU containing 80 mol % PCD was due to the high degree of crystallinity of this polymer.

Mechanical properties

Shore A/D hardness and tensile properties of all the PUs were studied after they were pressed at 70–140°C and approximately 10 MPa, and the numerical data for the polymers obtained in the melt are given in Table III.

As we can see from these data, the PU thermoplastic elastomers with soft segments derived from PTMO provided much higher tensile properties than the ones from polyesters. This was a result of the higher phase separation of hard and soft segments in comparison with polymers containing ester bonds in their structure. The higher elongation at break of the polyether-

based CPUs, in comparison with the polyester-based ones, was due to the greater flexibility of ether bonds in comparison with ester bonds. The tensile strength decreased and the elongation at break increased with a growing number of soft segments. The highest tensile strength, about 32 MPa, was obtained for CPUs containing 20 mol % PTMO, and the highest elongation at break, about 1200%, was obtained for a polymer containing 80 mol % polyether diol. For the poly(ester urethane)s, the increasing number of soft segments caused decreases in both the tensile strength and elongation at break. The best results, 19 MPa and 572%, were obtained for a CPU containing 20 mol % PCL. The X-ray diffraction analyses of the chosen polymers, conducted at room temperature, are shown in Figures 6 and 7 and in Table IV. The d-spacings were calculated from Bragg's relation, and the relative intensity, I/I_0, and the maxima of the peaks were

TABLE IV
X-Ray Analyses of PUs

PU	D	I/I_0
	9.19	33
	4.67	100
	4.62	26
PU-1	4.42	17
	4.14	17
	3.80	14
	3.33	
PU-20P	4.39	
PU-40P	4.44	
PU-60P	4.44	
PU-20P$_1$	4.39	
	9.05	56
	4.68	75
PU-40P$_1$	4.39	21
	4.17	100
	3.37	42
	9.45	53
	4.70	13
PU-60P$_1$	4.41	9
	4.18	100
	3.78	40
	3.13	18

determined with the XRAYAN (M. Marciniak, R. Diduszko; Warsaw, Poland) computer program. In Figure 6, we can see multiple sharp peaks in the range of $\theta = 7$–$14°$, with d-spacings between 9.19 and 3.33 Å, and these indicate well-crystallized nonsegmented PU-1.

For the CPUs, the increasing amount of polyether diol (see Fig. 6) in the polymer structure did not considerably influence their degree of crystallinity, and only one middle, broad reflection was observed in the range of $\theta = 9$–$12°$, corresponding to d-spacings of 4.39 and 4.44 Å, which represent a lower order of lateral chain packing.

The increasing content of polyester diol in the polymer structure caused the appearance of very sharp peaks in the range of $\theta = 8$–$12°$, corresponding to d-spacings of 9.05–3.13 Å, as shown in Figure 7 and Table IV. The CPU containing 20 mol % PCD displayed only one middle peak at $\theta = 8$–$14°$, corresponding to a d-spacing of 4.39 Å, and this result pointed to the semicrystalline character of this polymer.

CONCLUSIONS

The new aromatic-aliphatic linear PUs, composed of HHPE and MDI and obtained by polyaddition reactions, were hard, light yellow products when obtained in the melt or rubberlike products when obtained in solution. The nonsegmented PUs, possessing high T_m's of 216–222°C, were insoluble in common organic solvents at room temperature. They exhibited thermal stability up to 290°C and chemical resistance to dilute acids and alkali. The CPUs obtained in the melt from HHPE, MDI, and PTMO or PCD were strong, waxlike products, and some of them were soluble only in a phenol and CCE mixture. However, the segmented PUs obtained by the solution method were pale yellow thermoplastic masses, soluble in DMF, DMSO, and THF. Those CPUs containing soft segments derived from PTMO had softening temperatures of 60–140°C, and those with polyester soft segments had softening temperatures of 40–118°C, respectively. The poly(ether urethane)s exhibited a semicrystalline structure that was independent of the number of soft segments, whereas the poly(ester urethane)s were characterized by an increase in the degree of crystallinity with an increasing number of soft segments.

These CPU thermoplastic elastomers, with various amounts of soft segments derived from PTMO or PCD, are expected to find uses as elastic polymer materials.

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